Stable 2-Azabicyclo[2.2.0]hexa-2,5-diene Derivatives

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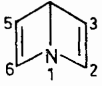
Summary Photolysis of perfluoro-tri- and -tetra-alkylpyridines gives stable products which contain isomers having the 2-azabicyclo[2.2.0]hexa-2,5-diene structure.

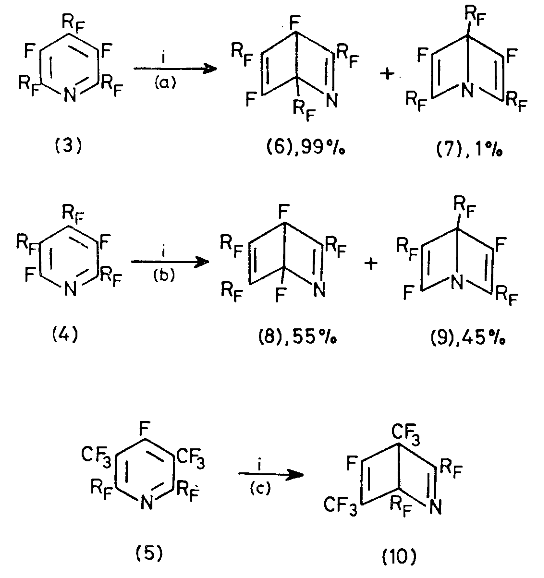
para-Bonded isomers of the pyridine system have been observed previously,[1-4] including very stable 1-azabicyclo-[2.2.0]hexa-2,5-diene (**1**) derivatives, which were obtained by the photolysis of fluorinated penta-alkylpyridines,[2-4] but the only example of the 2-azabicyclo[2.2.0]hexa-2,5-diene (**2**) system described was obtained as a very short-lived species, from the photolysis of pyridine.[1]

We now report the first very stable derivatives of the valence isomer (**2**), obtained by the photolysis of various perfluoro-tetra- and -tri-alkylpyridines, which we have synthesised previously. Other workers[2] have irradiated perfluoro-tetra- and -tri-ethylpyridines in solution, but did not isolate any valence isomers. Similarly, we have irradiated the pyridine derivatives (**3**)—(**5**) in solution in $CF_2ClCFCl_2$, or perfluoromethylcyclohexane, but did not detect any valence isomers. However, when we used a slow transference technique (0·5 mmHg air present), described previously,[5] the valence isomers (**6**)—(**10**) were obtained in the conversions indicated.



(1)

(2)



$R_F = CF(CF_3)_2$; i = 254 nm; (a) 37% conversion, (b) 46% conversion, and (c) 43% conversion.

Isomers (**6**) and (**7**) were separated by fractional distillation, isomer (**7**) being detected in a large-scale experiment. The structure of (**6**) follows from the ^{19}F n.m.r. spectrum which showed absorptions at δ 80·4 (CF=C) and 179·6, 186·7, 189·1, and 191·3 (each 1F, corresponding to 'tertiary' CF) p.p.m. (rel. to $CFCl_3$), in addition to resonances corresponding to CF_3. These data are consistent with those obtained from *para*-bonded isomers of aromatic diazines[5] and clearly indicate a bridgehead CF. Similarly, the i.r. spectrum of (**6**) showed bands at 1705 (C=N) and 1740 (C=C) cm^{-1}.† In contrast, the ^{19}F n.m.r. spectrum of the derivative (**7**) showed signals at δ 102·7 (2F, 2 × CF=C), 184·6 (1F) and 191·8 (2F) p.p.m. ('tertiary' CF). Isomers (**8**) and (**9**) were separated by distillation, although (**8**) was not isolated pure because some rearomatisation occurred during distillation in this case. Nevertheless, the ^{19}F n.m.r. data for (**8**) showed five separate 'tertiary' fluorine resonances and, the i.r. spectrum showed absorptions at 1705 (C=N) and 1735 (C=C) cm^{-1}. Similarly, the ^{19}F n.m.r. spectrum of the isomer (**9**) showed three 'tertiary' and two vinylic fluorine resonances and the i.r. spectrum showed a peak at 1742 (C=C) cm^{-1}. The structure of (**10**) followed in a similar manner.

All the isomers (**6**)—(**10**) rearranged at 160 °C to the corresponding pyridine derivatives (**3**)—(**5**) but only (**10**) slowly rearomatised on standing at room temperature over a period of several months, while (**6**)—(**9**) were completely unchanged after six months at room temperature. The 2-aza-isomer (**2**), rather than (**1**), is formed on photolysis of pyridine, although the product is very unstable,[1] and also, from the systems reported here, it is clear that the 2-aza skeleton is preferred. Furthermore, these observations are consistent with simple bond-energy summations which indicate a clear preference for (**2**) over (**1**). Therefore, the exclusive formation of derivatives of (**1**) from perfluoropenta-alkylpyridines, which has been described earlier,[2,4] demonstrates that the five perfluoroalkyl substituents dominate the choice between (**1**) and (**2**) in such systems. This stems from the obvious fact that structure (**2**) would contain four perfluoroalkyl groups attached to one cyclobutene ring whereas structure (**1**) would contain a maximum of three groups attached to one 4-membered ring.

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† Other workers have shown (M. G. Barlow, R. N. Haszeldine, and M. J. Kershaw, *J.C.S. Perkin I*, 1975, 2005) that, in bicyclo[2.2.0]hexadiene derivatives, absorption due to $-CF=C(CF_3)-$ occurs in this region.

[1] K. E. Wilzbach and D. J. Rausch, *J. Amer. Chem. Soc.*, 1970, **92**, 2178.
[2] M. G. Barlow, R. N. Haszeldine, and J. G. Dingwall, *J.C.S. Perkin I*, 1973, 1542.
[3] Y. Kobayashi and A. Ohsawa, *Tetrahedron Letters*, 1973, 2643.
[4] R. D. Chambers, R. Middleton, and R. P. Corbally, *J.C.S. Chem. Comm.*, 1975, 731.
[5] R. D. Chambers, J. R. Maslakiewicz, and K. C. Srivastava, *J.C.S. Perkin I*, 1975, 1130.